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(54) PRODUCTION OF CALCIUM DISPERSION AND FOOD CONTAINING THE SAME

(57)Abstract:
PURPOSE: To obtain a calcium dispersion, good in stability and hardly forming precipitates even when preserved for a long period by preparing fine calcium oxide particles from a sparingly water-soluble or water-insoluble calcium salt and a hydroxy acid, adding a hydrophilic emulsifying agent thereto and carrying out the dispersing treatment.
CONSTITUTION: This stable calcium dispersion is obtained by mixing and stirring a sparingly water-soluble or a water-insoluble calcium salt (calcium carbonate, etc.) and a hydroxy acid (citric acid) in a dispersion medium, producing a hydroxy acid salt of calcium having ≤1 μm average particle diameter, then adding a hydrophilic emulsifying agent having ≥10HLB thereto and carrying out the dispersing treatment for 20-30min with a usual dispersing machine.

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the calcium dispersing element which mixes and stirs water poor solubility or a water-insoluble nature calcium salt, and oxy acid in a dispersion medium, and includes the process which adjusts the mean particle diameter of a calcium particle to 1 micrometer or less, and the process at which HLB adds ten or more hydrophilic emulsifiers.
[Claim 2] The manufacture approach according to claim 1 that water poor solubility or a water-insoluble nature calcium salt is a calcium carbonate.
[Claim 3] The manufacture approach according to claim 1 or 2 that oxy acid is a citric acid.
[Claim 4] The manufacture approach according to claim 1 to 3 that the range of the convention (normal) ratio of water poor solubility or a water-insoluble nature calcium salt, and oxy acid is 1:1 to 1:1.2.
[Claim 5] The manufacture approach according to claim 1 to 4 that the water poor solubility in a dispersion medium or the concentration of a water-insoluble nature calcium salt is 5 - 13 % of the weight.
[Claim 6] The manufacture approach according to claim 1 to 5 that the concentration of the oxy acid in a dispersion medium is 10 - 20 % of the weight.
[Claim 7] The manufacture approach according to claim 1 that a dispersion medium is water.
[Claim 8] The manufacture approach according to claim 1 of adjusting the mean particle diameter of a calcium particle to 0.6 micrometers or less.
[Claim 9] The manufacture approach according to claim 1 that HLB adds ten or more hydrophilic emulsifiers by the weight ratio of 0.5-2 to a calcium carbonate.
[Claim 10] The manufacture approach according to claim 1 that a calcium dispersing element is what is used for drink addition.
[Claim 11] Food containing the calcium dispersing element manufactured by the manufacture approach according to claim 1.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the food containing the manufacture approach of a calcium dispersing element, and it.
[0002]
[Description of the Prior Art] Calcium is the bone of an animal, and a dental principal component, and is an element indispensable for a living thing. About Homo sapiens, intake of 0.6g [/day] calcium is needed also for 1.0g /and a small child the day by the adult. Although what is necessary is just to eat many small fish with the high content of calcium, cow's milk, soybeans, green leaf vegetables, etc. in order to take in the calcium of the above initial complements, in order to take in calcium efficiently, in recent years, the food which added calcium, i.e., calcium fortified food, is developed. For example, adding a water-soluble-organic-acids calcium salt to drinks, such as cow's milk, was performed conventionally. However, when the flavor of a drink was spoiled and protein was contained in a drink by adding such a water-soluble-organic-acids calcium salt, and sterilizing a drink, un-arranging [that proteinic coagulation took place by the sterilization inside of a plane, and dipping became impossible] had arisen.
[0003] The technique which adds mineral salt calcium like a calcium carbonate to a drink as an approach of solving the above-mentioned trouble was developed. JP,64-69513,A irradiates a supersonic wave what added sucrose fatty acid ester (generally called the sugar ester.) to the slurry-like calcium carbonate, makes a calcium-carbonate particle detailed, and is indicating the approach of making cow's milk, dissolved butter, etc. adding and distributing this. However, by the approach currently indicated with this official report, since the particle size of the calcium-carbonate particle made detailed was large, the good dispersibility of the calcium carbonate in a product was not acquired, and there was a fault that the calcium retention of the product after clarifier passage was low. Furthermore, in this approach, in order to make

cow's milk and butter distribute a calcium carbonate, high-speed agitators, such as a homogeneity machine and a homomixer, had to be used. Use of such a special device was what complicates the production process of a product.
[0004]
[Problem(s) to be Solved by the Invention] Therefore, this invention aims at offering the manufacture approach of a calcium dispersing element without the above-mentioned fault. Namely, this invention aims at offering the approach of carrying out [detailed]-izing of the calcium particle to sufficient extent distributing a calcium particle using the usual disperser by using a chemical reaction rather than being based on a mechanical shock. Moreover, this invention also makes it the purpose to offer the food containing a calcium dispersing element with good dispersibility.
[0005]
[Means for Solving the Problem] By making the calcium salt of water poor solubility or water-insoluble nature react with oxy acid, a calcium particle 1 micrometer or less is easily obtained for mean particle diameter, and this invention persons came to complete a header and this invention for the ability of stability to be made to distribute this calcium particle further, when HLB adds ten or more hydrophilic emulsifiers. That is, this invention mixes and stirs water poor solubility or a water-insoluble nature calcium salt, and oxy acid in a dispersion medium, and the manufacture approach of a calcium dispersing element including the process which adjusts the mean particle diameter of a calcium particle to 1 micrometer or less, and the process at which HLB adds ten or more hydrophilic emulsifiers is offered. Moreover, this invention offers the food containing the calcium dispersing element manufactured by the above-mentioned manufacture approach.
[0006] Although not necessarily adhered to the specific theory, a calcium carbonate (calcium salt of water poor solubility or water-insoluble nature) and a citric acid (oxy acid) are taken for an example, and the reaction mechanism of the calcium salt of the water poor solubility in this invention or water-insoluble nature and oxy acid is explained below.
[0007] a calcium carbonate -- a citric acid -- a reaction -- calcium citrate -- generating -- although -- this -- fusibility -- a chelate compound -- it is -- [- OOCCH -- two -- C -- (-- OH --) (COO-) -- CH -- two -- COO -] -- [-- calcium -- two -- + --] -- CO -- three -- poor solubility -- a salt -- a chelate compound -- it is -- [- OOCCH -- two -- C -- (-- OH --) (COO-) -- CH -- two -- COO -] -- two -- calcium -- two -- + -- three - four -- H -- two -- O -- mixture -- it is -- ** -- thinking -- having -- **** . However, both ratio changes with the ratio of concentration of calcium-carbonate concentration, citric-acid concentration, a calcium carbonate, and a citric acid, solution temperature, etc. Precipitate of the calcium citrate which uses the chelate compound of the above-mentioned poorly soluble salt as a principal component is made to produce in this invention by making a calcium carbonate

and a citric acid react under a suitable reaction condition. It atomizes precipitate of the calcium citrate to generate and it can prepare a stable calcium dispersing element using this.

[0008] Hereafter, this invention is explained to a detail. It sets to this invention, water poor solubility or a water-insoluble nature calcium salt, and oxy acid are mixed and stirred in a dispersion medium, and the mean particle diameter of a calcium particle is adjusted to 1 micrometer or less. As water poor solubility or a water-insoluble nature calcium salt, a calcium carbonate, calcium phosphate, calcium hydrogenphosphate, a calcium hydroxide, a calcium sulfate, and calcium citrate can be used, and it is good preferably to use a calcium carbonate.

[0009] Moreover, although what reacts with water poor solubility or a water-insoluble nature calcium salt, and can generate water poor solubility or a water-insoluble nature calcium oxy acid salt as oxy acid can be used and a citric acid, a tartaric acid, a lactic acid, a gluconic acid, a malic acid, etc. can be illustrated, the citric acid which has two or more carboxyl groups is desirable. As a dispersion medium, it is desirable to use water.

[0010] What is necessary is to add water poor solubility or a water-insoluble nature calcium salt, and oxy acid, to mix, and just to adjust the mean particle diameter of a calcium particle to 1 micrometer or less, stirring a dispersion medium by dispersers, such as a homomixer and a my colloider. As a convention (normal) ratio of water poor solubility or a water-insoluble nature calcium salt, and oxy acid, 1:1 to 1:1.2 is desirable, and 1:1 to 1:1.15 is more desirable. The problem that unreacted water poor solubility or a water-insoluble nature calcium salt will remain as a big and rough particle if the convention ratio of oxy acid to water poor solubility or a water-insoluble nature calcium salt is smaller than 1 arises, and if larger than 1.2, pH of the calcium dispersing element obtained by unreacted oxy acid becomes high, and in case it adds for food, the problem that pH adjustment must be carried out will arise. The water poor solubility in a dispersion medium or the concentration of a water-insoluble nature calcium salt has 5 - 13 desirable % of the weight, and its 10 - 13 % of the weight is more desirable. The problem that the original purpose will not be reached in case the calcium concentration of the calcium dispersing element obtained becomes low and addition strengthening of the calcium is carried out at food if the water poor solubility in a dispersion medium or the concentration of a water-insoluble nature calcium salt is lower than 5 % of the weight arises, if higher than 13 % of the weight, the generation ratio of the chelate compound of a poorly soluble salt will become excessive, and the problem that extent of decentralization of a calcium particle falls will arise. For example, when water poor solubility or a water-insoluble nature calcium salt is a calcium carbonate, the calcium-carbonate concentration in a dispersion medium has 5 - 13 desirable % of the weight, and its 10 - 13 % of the weight is more desirable. The concentration of the oxy acid in a dispersion

medium has 10 - 20 desirable % of the weight, and its 15 - 20 % of the weight is more desirable. The problem that the original purpose will not be reached in case the calcium concentration of the calcium dispersing element obtained becomes low and addition strengthening of the calcium is carried out at food if the concentration of the oxy acid in a dispersion medium is lower than 10 % of the weight arises, and if higher than 20 % of the weight, even if it makes it the concentration beyond this, since the generation percentage of the chelate compound of a poorly soluble salt will not change, the problem of being disadvantageous will produce it economically. For example, when oxy acid is a citric acid, the citric-acid concentration in a dispersion medium has 10 - 20 desirable % of the weight, and its 15 - 20 % of the weight is more desirable. Moreover, distribution is good to carry out preferably, until it is set to 0.6 micrometers or less until the mean particle diameter of a calcium particle is set to 1 micrometer or less. If the mean particle diameter of a calcium particle is larger than 1 micrometer, the problem that extent of decentralization of a calcium particle falls will arise. For example, if the water poor solubility in a dispersion medium or the mixture of a water-insoluble nature calcium salt and oxy acid is stirred for 10 - 30 minutes at the rotational frequency of the solution temperature of 20-30 degrees C, and 10,000 - 12,000rpm, mean particle diameter of the calcium particle in a dispersion medium can be set to 1 micrometer or less. Preferably, the above-mentioned mixture is stirred for 20 - 30 minutes at the rotational frequency of the temperature of 20-25 degrees C, and 10,000 - 12,000rpm.

[0011] HLB adds ten or more hydrophilic emulsifiers to the calcium suspension obtained as mentioned above. HLB can use sucrose fatty acid ester and polyglyceryl fatty acid ester as ten or more hydrophilic emulsifiers. The addition of the above-mentioned emulsifier has the desirable weight ratio of 0.5-2 to water poor solubility or a water-insoluble nature calcium salt, and its weight ratio of 0.8-1.5 is more desirable. The problem that there is little effectiveness over the amount used and it is not economical if there are more additions of an emulsifier than a double quantitative ratio arises, and if fewer than 0.5-fold quantitative ratio, the problem that decentralization of a calcium particle becomes inadequate will arise. In the case of addition of the above-mentioned emulsifier, the water of the weight ratio of 3-5 is added to the mixed stirring liquid of a calcium salt and oxy acid. By addition of water, the above-mentioned emulsifier can fully be distributed and a calcium dispersing element can be manufactured efficiently.

[0012] After HLB adds ten or more hydrophilic emulsifiers, calcium suspension is distributed further. It is good to be able to perform distribution using the above homomixers, a my colloider, etc., and to carry out for 20 - 30 minutes. Thereby, a stable calcium dispersing element can be obtained.

[0013] Calcium fortified food can be manufactured by making food add and distribute the above-mentioned calcium dispersing element. As food which

adds a calcium dispersing element, food, such as drinks, such as cow's milk, soybean milk, a milk beverage, fruit juice, juice, a soft drink, and tea, soup, and a stew, can be mentioned. The addition of the calcium to 100g of food is an amount which is preferably set to 100-150mg, and can add 50-200mg of calcium dispersing elements for food. Since the milk calcium dispersing element manufactured by the approach of this invention has good distributed stability, food can be made to distribute it using a line mixer, a batch type mixing tank, etc.

[0014] Thus, the manufactured calcium fortified food may perform sterilization processing, applying an elevated temperature and high pressure, and when calcium fortified food is a drink, it may remove a foreign matter using a clarifier etc. Hereafter, although an example explains this invention concretely, the range of this invention is not limited to this.

[0015]

[Example]

[Example 1]

(1) Preparation of calcium suspension Calcium carbonate (Shiroishi calcium trade name koro KARUN) 150g Citric acid (Takeda Chemical Industries, Ltd. make) 210g Water (tap water) 1140g While stirring water by the homomixer (table-top-type 10,000rpm) in 1500g ordinary temperature The calcium carbonate and the citric acid were added and particle size distribution were measured with time. The relation between the mixing time after adding a calcium carbonate and a citric acid in water, and the mean particle diameter of a calcium particle is shown in the following table 1.
 [0016]

[Table 1]

Table 1 ---------- ---------- mixing time (minute) 1 10 20 30 particle size (micrometer) 6.5 6.3 0.4 The calcium particle with a mean particle diameter of 1 micrometer or less was obtained by the mixing time for 0.3 ---------- ---------- 20 minutes.

[0017] (2) Preparation of calcium dispersion liquid 20% (mixing time 30 minutes) of calcium suspension prepared by (1) Sugar ester F-160 (Dai-Ichi Kogyo Seiyaku Co., Ltd. make) 3% Water (tap water) 77% Total Mixed liquor of the 100% above When it distributed for 20 minutes by the homomixer (table-top-type 10,000rpm) like actuation of (1), the calcium particle with a mean particle diameter of 0.4 micrometers was obtained.

[0018] (3) In addition, the calcium dispersion liquid prepared by (2) to the addition skimmilk (9.0 % of the weight of SNF(s)) to the food of calcium dispersion liquid were saved by standing with the milk bottle so that it might become 10% (equivalent to amount % of 120mg of calcium strengthening) of concentration, and the existence of precipitate formation was observed for three days. The result is shown in Table 2.

[0019]

[Table 2] Table 2 ---------- standing days(Sun.) 1 2 Existence of 3

---------- precipitate formation - - **---------- ---- -:
There is no precipitate.
**: Precipitate is accepted slightly.
[0020] [Example 2]
(1) It carried out like (1) of the preparation example 1 of calcium suspension.
(2) Preparation of calcium dispersion liquid Calcium suspension prepared by (1) (mixing time 30 minutes) 20% Polyglyceryl fatty acid ester (the TAIYO KAGAKU CO., LTD. make, HLB12) 2% Water (tap water) 78% Total Mixed liquor of the 100% above When it distributed for 20 minutes by the homomixer (table-top-type 10,000rpm) like actuation of (1), the calcium particle with a mean particle diameter of 0.2 micrometers was obtained.
(3) In addition, the calcium dispersion liquid prepared by (2) to the addition skimmilk (9.0 % of the weight of SNF(s)) to the food of calcium dispersion liquid were saved by standing with the milk bottle so that it might become 10% (equivalent to amount % of 120mg of calcium strengthening) of concentration, and the existence of precipitate formation was observed for three days. The result is shown in Table 3.
[0021]
[Table 3] Table 3 ---------- standing days(Sun.) 1 2 Existence of 3 ---------- precipitate formation - - -** ---------- **:
When shaken lightly, precipitate distributed.
[0022] [Example 3]
(1) With the presentation below preparation of calcium suspension, and the rotational frequency, calcium suspension was prepared in ordinary temperature using the homomixer.
Calcium carbonate Citric acid Water Rotational frequency A citric acid / koro KARUN (koro KARUN) (weight ratio) (convention ratio)
** 150 g 150 g 1200 g 3000 rpm 1.0 0.8 ** ** ** 6000 rpm ** ** ** ** ** 10000 rpm ** **** 150 g 180 g 1170 g 10000 rpm 1.2 0.9 ** 150 g210 g 1140 g 10000 rpm 1.41.1 calcium carbonates and citric acid The mixing time after adding in water, the mean particle diameter of a calcium particle, and relation with pH of calcium suspension are shown in the following table 4.
[0023]
[Table 4]
Table 4 ---------- ---------- mixing time 1 (minute) 5 10 15 20 25 30 35 40 ---------- ** Particle size 3.18 - 2.66 - 2.69 - 2.52 - - (micrometer) 3000rpm pH 3.92 4.35 4.57 4.70 5.57 5.90 5.97 - - Particle size 4.12- 2.84 - 2.92 -2.82-- (micrometer) 6000rpm pH 3.80 4.30 4.53 4.68 4.72 5.94 6.20 6.41 6.54** particle size 2.71- 2.19 -2.30- - - - micrometer10000rpm pH 3.90 4.32 4.60 6.34 7.42 7.65 7.66 - - ** Particle size 4.20 - 3.30 - 3.08- - - - (micrometer) 10000rpm pH 3.79 4.13 4.31 5.55 7.36 7.78 - - - Particle size 6.52 - 6.28 - 0.43 0.34 - - - (micrometer) 10000rpm pH 3.56 3.77 3.91 4.00 3.80 4.23 - - -

---------- [0024] (2) Preparation of calcium dispersion liquid Calcium suspension prepared by (1) ** (mixing time 25 minutes) 10g Sugar ester F-160 (Dai-Ichi Kogyo Seiyaku Co., Ltd. make) 1g Water (tap water) 89g Total Mixed liquor of the 100g above When it distributed for 20 minutes by the homomixer, the calcium particle with a mean particle diameter of 0.4 micrometers was obtained.

[0025]

[Effect of the Invention] The calcium dispersing element which has good distributed stability by this invention, without using a facility **** in whether they are size, such as a mill, is obtained. Even if it saves the food containing the calcium dispersing element obtained by this invention for a long period of time, it is hard to produce precipitate, and it has advantages, like that the calcium content of food is high, and the loss of calcium is economical few. Furthermore, since it is possible to make food distribute calcium even if it does not use special dispersers, such as a homogeneity machine and a homomixer, if the calcium dispersing element of this invention is used, it is possible to simplify the production process of calcium fortified food, and plant-and-equipment investment can also be pressed down to the minimum.

[Translation done.]